

Rate Coefficient for the Gas-Phase OH + CHF=CF₂ Reaction between 212 and 375 K

MUNKHBAYAR BAASANDORJ,^{1,2} JAMES B. BURKHOLDER¹

¹Earth System Research Laboratory, Chemical Sciences Division, National Oceanic and Atmospheric Administration, Boulder, CO 80305

²Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

Received 27 May 2016; revised 30 June 2016; accepted 11 July 2016

DOI 10.1002/kin.21027

Published online 8 September 2016 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Rate coefficients, $k(T)$, for the OH + CHF=CF₂ (trifluoroethylene, HFO-1123) gas-phase reaction were measured under pseudo-first-order conditions using pulsed laser photolysis to produce OH radicals and pulsed laser induced fluorescence to measure the OH radical temporal profile. Rate coefficients were measured over the temperature range 212–375 K at total pressures between 20 and 500 Torr (He, N₂ bath gas). The rate coefficient was found to be independent of pressure over this range of pressure with a temperature dependence that is described by the Arrhenius expression $(3.04 \pm 0.30) \times 10^{-12} \exp[(312 \pm 25)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with $k(296 \text{ K})$ measured to be $(8.77 \pm 0.80) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (quoted uncertainties are 2σ and include estimated systematic errors). Rate coefficients for the reaction of CHF=CF₂ with ¹⁸OH and OD were also measured as part of this study at 296 and 373 K and a total pressure of ~25 Torr (He). The isotope measurements were used to evaluate the observed OH radical regeneration. CHF=CF₂ is a very short-lived substance with an atmospheric lifetime of ~1 day with respect to OH reactive loss, whereas the actual lifetime of CHF=CF₂ will depend on the time and location of its emission. The global warming potential for CHF=CF₂ on the 100-year time horizon (GWP₁₀₀) was estimated using the present results and a lifetime correction factor to be 3.9×10^{-3} . © 2016 Wiley Periodicals, Inc. *Int J Chem Kinet* 48: 714–723, 2016

INTRODUCTION

CHF=CF₂ (trifluoroethylene, HFO-1123) is a hydrofluoroolefin that has recently been proposed as a possible replacement for high-global warming potential (GWP) refrigerant compounds. The commercial use of hydrofluoroolefins (HFOs) leads to their direct release into the atmosphere. HFOs are potent

Correspondence to: J. B. Burkholder; e-mail: James.B.Burkholder@noaa.gov

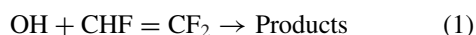
Present address of Munkhbayar Baasandorj: Utah Division of Air Quality, Salt Lake City, UT 84114.

Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

© 2016 Wiley Periodicals, Inc.

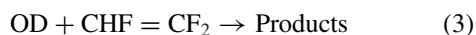
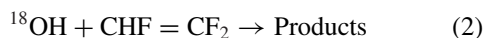
greenhouse gases with strong infrared absorption in the atmospheric window region, but their impact on climate will strongly depend on the compounds atmospheric lifetime [1]. Hydrofluoroolefins are attractive replacement compounds from an atmospheric chemistry perspective due to their high reactivity with the OH radical and expected short atmospheric lifetimes, which minimizes their climate impact. A comprehensive understanding of the atmospheric chemistry of a HFO replacement compound is a key component in the determination of its acceptability.

The gas-phase reaction of CHF=CF₂ with the OH radical:



is expected to proceed via OH radical addition to the carbon-carbon double bond and the formation of a semistable OH-CHF=CF₂ radical adduct. In the atmosphere, this adduct will react rapidly with O₂ to irreversibly form a hydroxypetroxy radical.

In this study, rate coefficients for reaction (1) were measured over a range of temperature (212–375 K) at total pressures between 20 and 500 Torr (He, N₂ bath gas) using an absolute kinetic method. OH radical regeneration was observed in our study under low-pressure conditions as was also observed in our previous study of the OH + CH₂=CHF and CH₂=CF₂ reactions [2]. In our previous study, it was suggested that the observed OH regeneration was most likely due to the reaction of O₂ with an excited HO-HFO adduct. The present kinetic study provides an opportunity to compare the efficiency of OH radical regeneration in a similar but more highly fluorinated compound. As part of this work, rate coefficients for reaction (1) were also measured using the ¹⁸OH and OD isotopically substituted radicals:



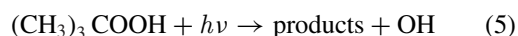
to aid the interpretation and the identification of the mechanism and conditions under which OH regeneration occurs. Chen et al. [3] has reported rate coefficients for reaction (1) that were obtained using a relative rate method at temperatures over the range 253–328 K. The present results, which were obtained over an extended temperature range, are compared with the results of Chen et al. The present study contributes to the fundamental studies needed to develop a better understanding of the trends in OH radical reactivity of HFOs.

EXPERIMENTAL

Rate coefficients for the OH + CHF=CF₂ reaction were measured using a pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique. The experimental methods and apparatus have been used extensively in our laboratory and have been described recently elsewhere [4,5]. Only the details relevant for the current study are presented below. In addition to the kinetic measurements, the infrared absorption spectrum of CHF=CF₂ at 298 K and its 185-nm absorption cross section were measured as part of this work. The kinetic and absorption apparatus and methods are described separately below.

OH Rate Coefficient Measurements

The experimental apparatus consisted of a small volume reactor where the OH radicals were produced and detected. Pulsed lasers were used to produce and excite the OH radical. Reaction rate coefficients were measured under pseudo-first-order conditions in OH, [CHF=CF₂] > [OH] with the CHF=CF₂ concentration measured online using Fourier transform infrared (FTIR) spectroscopy and UV (185 nm) absorption. OH radicals were produced using 248 nm (KrF excimer laser) pulsed laser photolysis of H₂O₂ or (CH₃)₃COOH:



H₂O₂ was used for measurements at temperatures ≥250 K, whereas (CH₃)₃COOH was used at all temperatures. The initial OH radical concentration, [OH]₀, was estimated from the precursor concentration; its absorption cross section at 248 nm [6,7] and the photolysis laser fluence (5–23 mJ cm⁻² pulse⁻¹ were used over the course of the study). The OH precursor concentrations were estimated from the pseudo-first-order rate coefficients measured in the absence of CHF=CF₂ and were in the range (0.3–2.0) × 10¹⁴ molecule cm⁻³ for H₂O₂ and (0.67–3.76) × 10¹⁴ molecule cm⁻³ for (CH₃)₃COOH.

For the OD and ¹⁸OH kinetic experiments, the radicals were produced using 248-nm pulsed laser photolysis of O₃ in a He bath gas to produce O(¹D) followed by its reaction with D₂O or H₂¹⁸O, respectively (see Baasandorj et al. [2]). The water vapor concentration (D₂O or H₂¹⁸O) was estimated from gas flows and pressures to be ~2 × 10¹⁶ molecule cm⁻³, which was sufficient to remove 99% of the O(¹D) produced within

1 μ s. The O₃ concentration in these experiments was estimated to be $\sim 1 \times 10^{13}$ molecule cm⁻³.

OH radical fluorescence was detected following pulsed laser excitation in the $A^2\Sigma^+ \leftarrow X^2\Pi(v=0)$ transition near 282 nm with the frequency doubled output from a pulsed Nd:YAG pumped dye laser. ¹⁸OH and OD were excited using transitions near 282.07 and 287.6 nm, respectively. OH temporal profiles were measured by varying the delay between the photolysis and the probe lasers (i.e., the reaction time) between 10 and 10,000 μ s.

OH temporal profiles were analyzed using the integrated rate equation:

$$\ln\left(\frac{[\text{OH}]_t}{[\text{OH}]_0}\right) = \ln\left(\frac{S_t}{S_0}\right) = -(k[\text{CHF}=\text{CF}_2] + k_d)t = -k't \quad (\text{I})$$

where S_t is the measured OH signal at time t , $[\text{CHF}=\text{CF}_2]$ is the $\text{CHF}=\text{CF}_2$ concentration, and k' and k_d are the first-order rate coefficients for loss of OH in the presence and absence of $\text{CHF}=\text{CF}_2$, respectively. k' values were obtained as the slope of a least-squares fit of S_t versus time. k_d represents the loss of OH, due primarily to its reaction with the OH precursor and diffusion out of the detection volume, with values in the range 50 to ~ 500 s⁻¹. OH temporal profiles were measured over a range of $\text{CHF}=\text{CF}_2$ concentration at each temperature and pressure. The $\text{CHF}=\text{CF}_2$ concentration was measured online using infrared absorption, either before or after the LIF reactor, and UV absorption prior to the LIF reactor. The absorption measurements were performed at 296 K. The $\text{CHF}=\text{CF}_2$ concentration determined from the absorption measurements was scaled to accurately, $\pm 1\%$, account for differences in pressure (5–10%) between the absorption cells and LIF reactor. Scaling was also applied to account for the difference in $\text{CHF}=\text{CF}_2$ number density between the room temperature absorption cells and the LIF reactor, which were made using the measured temperatures and the ideal gas law and accurate to $\pm 1\%$. $k(T)$ was determined from the slope of k' versus $[\text{CHF}=\text{CF}_2]$. The Arrhenius parameters, A and E/R , were obtained from a precision weighted linear least-squares fit of the Arrhenius expression:

$$\ln(k(T)) = \ln(A) - \frac{E}{RT} \quad (\text{II})$$

Absorption Cross Section Measurements

The infrared absorption spectrum of $\text{CHF}=\text{CF}_2$ was recorded using a FTIR equipped with a mercury

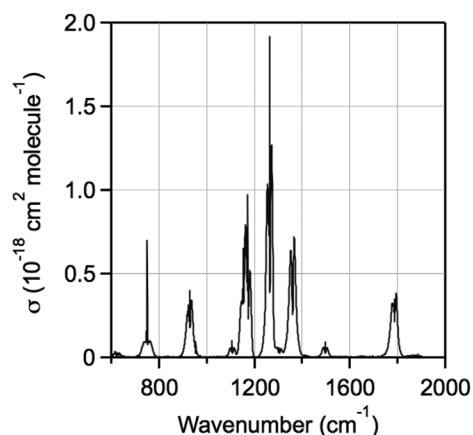


Figure 1 Infrared absorption spectra of $\text{CHF}=\text{CF}_2$ at 296 K measured in this work at 1 cm⁻¹ resolution using a FTIR. Integrated band strengths are reported in Table I and a digitized spectrum is available in the Supporting Information.

cadmium telluride (MCT) detector and multipass cell (485 cm optical pathlength, 500 cm³ volume) between 500 and 4000 cm⁻¹ at a spectral resolution of 1 cm⁻¹.

$\text{CHF}=\text{CF}_2$ was added to the absorption cell from dilute mixtures, and its concentration was varied over the range $(3.60\text{--}6.36) \times 10^{15}$ molecule cm⁻³ with 20 absorption spectra recorded. The absorption spectra, $A(\nu)$, obeyed Beer's law:

$$A(\nu) = -\ln\left(\frac{I}{I_0}\right) = \sigma(\nu)L[\text{CHF}=\text{CF}_2] \quad (\text{III})$$

where I and I_0 are the transmitted intensity through the cell with and without $\text{CHF}=\text{CF}_2$ present, $\sigma(\nu)$ is the $\text{CHF}=\text{CF}_2$ absorption cross section, and L is the pathlength of the absorption cell. The measured spectra were independent of total pressure between 20 and 600 Torr He. The spectrum is shown in Fig. 1 and integrated band strengths determined from a linear least-squares fit of the recorded spectra are given in Table I.

Table I Infrared Absorption Band Strengths for $\text{CHF}=\text{CF}_2$ at 296 K

Integration Range (cm ⁻¹)	Band Strength (10 ⁻¹⁸ cm ² molecule ⁻¹ cm ⁻¹)
700–800	5.12 \pm 0.05
870–980	10.1 \pm 0.04
1060–1210	25.4 \pm 0.09
1210–1440	55.7 \pm 0.14
1455–1535	1.78 \pm 0.05
1700–1910	12.5 \pm 0.03

*The uncertainties are 2 σ precision from the linear least-squares analysis of the integrated absorbance versus concentration.

A digitized spectrum is provided in the Supporting Information.

Absorption measurements at 184.9 nm were made using a Hg pen-ray lamp light source, a 100 cm long absorption cell, and a solar blind photodiode with a 185 nm band-pass filter. The same setup was used for the online measurements during the kinetic experiments. The 184.9 nm absorption cross section was determined under static conditions using absolute pressure measurements with a manometrically prepared mixture (0.01–0.06% CHF=CF₂ in He). The CHF=CF₂ concentrations were in the range $(0.28\text{--}2.06) \times 10^{15}$ molecule cm⁻³ and the measured absorbance obeyed Beer's law. A linear least-squares analysis of *A* versus [CHF=CF₂] yielded a 185 nm absorption cross section of $(5.78 \pm 0.05) \times 10^{-18}$ cm² molecule⁻¹.

Materials

He (UHP; 99.999%), N₂ (UHP; 99.99%), N₂ (UHP; O₂ <0.5 ppm), O₂ (UHP; 99.99%), and (CH₃)₃COOH (50 wt%) were used as supplied. H₂O₂ (>95% mole fraction) and (CH₃)₃COOH were introduced into the gas flow just prior to entering the LIF reactor by passing a small flow of He through a bubbler containing the liquid sample at 273 K. The CHF=CF₂ (98% stated purity) sample was degassed in several freeze-pump-thaw cycles before use. Dilute mixtures of CHF=CF₂ in a He bath gas were prepared manometrically in 12-L Pyrex bulbs. The CHF=CF₂ mixtures were stable over the course of the study, as determined by periodic infrared absorption measurements. Gas flows were measured with calibrated electronic mass flow meters and pressures were measured using 10, 100, and 1000 Torr capacitance manometers. The gas flow velocities in the kinetic measurements were in the range 5–15 cm s⁻¹, such that a fresh sample of gas was in the reaction volume for each photolysis pulse. Quoted uncertainties in this paper are 2σ unless stated otherwise.

RESULTS AND DISCUSSION

A summary of the experimental conditions and rate coefficients obtained for reactions (1)–(3) is given in Tables II–III, respectively. Rate coefficients for reaction (1) were determined over the temperature range 212–375 K at total pressures between 20 and 500 Torr (He, N₂). The OH radical temporal profiles measured for reaction (1) obeyed Eq. (1), i.e., pseudo-first-order, at pressures >100 Torr (He) and at 300 Torr (N₂) and representative profiles are shown in Fig. 2. The OH profiles recorded at lower pressure, ~20 Torr (He),

showed systematic deviations from pseudo-first-order behavior on the timescale of our measurements that provide evidence for OH radical regeneration, which is discussed further below. The rate coefficients reported in Table II were obtained under conditions where no OH radical regeneration was observed. On the basis of these measurements, there was no dependence of the rate coefficient on pressure observed in this study.

Figure 3 shows the second-order plots for reaction (1) obtained at room temperature and the temperature extremes of this study. Measurements were made over a wide range of CHF=CF₂ concentration and under a range of experimental conditions (see Table I) that yielded highly consistent results. Rate coefficients for the ¹⁸OH and OD reactions measured in this work were obtained over a more limited range of conditions than for reaction (1) (see Table III). The ¹⁸OH and OD temporal profiles measured with and without O₂ added to the reaction mixture displayed single exponential behavior with no evidence for ¹⁸OH or OD radical regeneration, respectively. Representative ¹⁸OH temporal profiles measured under conditions that were expected to most likely lead to ¹⁸OH radical regeneration, 373 K and 20 Torr (He), are shown in Fig. 4. The second-order kinetic results from the ¹⁸OH experiments are included in Fig. 3 and were found to be in good agreement with the ¹⁶OH results obtained at ≥100 Torr (He, N₂). The ¹⁸OH and ¹⁶OH data were combined in the final kinetic analysis.

The rate coefficients for reactions (1)–(3) were determined from a precision weighted linear least-squares fit of all data obtained at a given temperature using Eq. (1). The room temperature rate coefficients for reactions (1)–(3) were determined to be nearly identical with values of 8.77 ± 0.02 , 8.77 ± 0.16 , and 8.95 ± 0.08 (10⁻¹² cm³ molecule⁻¹ s⁻¹), respectively. The 373-K rate coefficients for reaction (1)–(3) also agreed to within the measurement uncertainty. The rate coefficient results for reactions (1)–(3) are plotted in Fig. 5 and are well-represented by a simple Arrhenius expression. A precision weighted linear least-squares fit of all ¹⁶OH and ¹⁸OH data combined over the temperature range 215–375 K yielded the Arrhenius expression $(3.04 \pm 0.06) \times 10^{-12} \exp[(312 \pm 25)/T]$ where the quoted uncertainties are from the precision of the fit. Reaction (1) exhibits a weak negative temperature dependence that is consistent with an OH addition to the carbon-carbon double bond reaction mechanism.

The precision of the kinetic measurements was better than 3% and the uncertainty in the experimental parameters was low with estimated uncertainties of ±1% in pressure, ±2% in gas flow rates, and ±1 K in temperature. Three methods were used to determine [CHF=CF₂] including measured gas flow rates

Table II Summary of Experimental Conditions and Rate Coefficients Obtained for the $^{16}\text{OH} + \text{CHF} = \text{CF}_2$ Reaction

$T(\text{K})$	$P(\text{Torr})$	Bath Gas	$V(\text{cm s}^{-1})$	Laser Fluency ($\text{mJ cm}^{-2} \text{ pulse}^{-1}$)	[Precursor] ($10^{14} \text{ molecule cm}^{-3}$)	[OH] ₀ ($10^{11} \text{ molecule cm}^{-3}$)	[CHF=CF ₂] ($10^{14} \text{ molecule cm}^{-3}$)	k^c ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
215	300	He	5.8	21	0.67 ^a	0.35	0.80–6.65	12.91 ± 0.09
226	300	N ₂	5.1	20	1.31 ^a	0.65	0.95–6.83	12.15 ± 0.50
230	300	He	6.0	23	0.93 ^a	0.55	0.74–7.16	11.64 ± 0.08
230	300	He	6.0	23	0.93 ^a	0.55	0.77–6.83	11.85 ± 0.31 ^d
245	300	He	6.4	21	1.76 ^a	0.42	0.47–7.74	$k_2(230 \text{ K}) = 11.73 \pm 0.14^e$ 10.85 ± 0.09
250	200	N ₂	5.8	21	3.76 ^a	0.85	0.90–8.10	$k_2(245 \text{ K}) = 10.85 \pm 0.09^e$ 11.16 ± 0.18
250	200	N ₂	5.8	21	3.76 ^a	0.85	0.94–8.00	11.23 ± 0.21 ^d
260	300	He	6.8	22	0.73 ^a	0.40	0.83–7.61	$k_2(250 \text{ K}) = 11.15 \pm 0.18^e$ 10.07 ± 0.11
275	300	He	5.9	24	1.29 ^a	1.43	0.16–8.86	9.47 ± 0.11
275	300	He	5.9	24	1.29 ^a	1.43	0.46–6.41	9.43 ± 0.13 ^d
296	100	He	10.2	9.0	0.3 ^b	0.60	0.31–9.15	$k_2(275 \text{ K}) = 9.46 \pm 0.08^e$ 8.86 ± 0.19
296	100	He	10.1	8.1	0.3 ^b	0.54	0.26–9.86	8.70 ± 0.15
296	100	He	10.0	8.1	0.3 ^b	0.54	0.57–11.70	8.60 ± 0.08 ^d
296	300	He	5.9	7.9	0.8 ^b	1.36	0.26–10.26	8.76 ± 0.16
296	300	He	5.9	7.9	0.8 ^b	1.36	0.27–9.71	8.78 ± 0.04 ^d
296	300 (320)	He	5.5	28	1.33 ^a	0.93 (t-but)	0.50–8.79	8.89 ± 0.23
296	300	N ₂	6.2	5.5	1.01 ^b	1.26	0.73–7.68	9.00 ± 0.13
296	300	N ₂	6.2	5.5	1.01 ^b	1.26	0.16–6.10	8.92 ± 0.10 ^d
320	300	He	6.0	13.0	0.81 ^b	4.32	0.67–10.50	$k_2(296 \text{ K}) = 8.77 \pm 0.02^e$ 8.03 ± 0.04
340	300	He	6.0	13.0	1.21 ^b	3.55	0.52–8.40	7.52 ± 0.12
345	300	N ₂	6.2	6	1.47 ^b	1.98	2.51–11.10	7.69 ± 0.12
357	300	He	6.5	11.0	1.19 ^b	3.02	0.54–11.00	7.40 ± 0.08
357	500	He	6.0	11.0	1.11 ^b	2.81	0.98–8.46	7.24 ± 0.07
375	300	He	7.9	9.5	1.62 ^b	3.49	0.11–12.20	$k_2(357 \text{ K}) = 7.33 \pm 0.04^e$ 7.02 ± 0.08

Continued

Table II Continued

<i>T</i> (K)	<i>P</i> (Torr)	Bath Gas	<i>V</i> (cm s ⁻¹)	Laser Fluency (mJ cm ⁻² pulse ⁻¹)	[Precursor] (10 ¹⁴ molecule cm ⁻³)	[OH] ₀ (10 ¹¹ molecule cm ⁻³)	[CHF=CF ₂] (10 ¹⁴ molecule cm ⁻³)	<i>k</i> ^c (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)
375	300	He	7.9	9.5	1.62 ^b	3.49	1.54–12.40	6.90 ± 0.08 ^d
375	500	He	6.3	9.6	1.17 ^b	2.52	0.13–12.00	6.87 ± 0.05
374	300	N ₂	5.1	6.9	1.42 ^b	2.22	1.21–14.00	6.94 ± 0.06
374	300	N ₂	5.1	6.9	1.42 ^b	2.22	2.4–11.20	7.06 ± 0.09 ^d
								<i>k</i> ₂ (375 K) = 7.01 ± 0.05 ^e

^a(CH₃)₃COOH was used as the OH precursor.^bH₂O₂ was used as the OH precursor photolyte.^cThe quoted uncertainties are 2σ precision of the linear least-squares fit of *k* versus [CHF=CF₂].^dO₂ added to the reaction mixture with concentrations between (0.9–4.9) × 10¹⁶ molecule cm⁻³.^eDetermined from a weighted linear least-squares fit to all (*k* – *k*₀) versus [CHF=CF₂] at this temperature.

and pressures as well as online UV and infrared absorption measurements. The agreement between these measurements was better than 5% under all conditions. The absorption measurements made before and after the LIF reactor also agreed to better than 5%, which indicates that there was no significant loss of CHF=CF₂ in the gas flow through the apparatus. The overall root mean square (RMS) uncertainty in *k*₁(*T*) is estimated to be ~6%, independent of temperature. It is worth noting that the temperature dependence of the rate coefficient is actually determined more accurately than the absolute value. Our recommended Arrhenius expression for reaction (1) is $(3.04 \pm 0.18) \times 10^{-12} \exp[(312 \pm 25)/T]$ cm³ molecule⁻¹ s⁻¹, where the estimated absolute uncertainty is included in the preexponential factor.

There is a previous relative rate study of reaction (1) available in the literature that can be compared with the present results. Chen et al. [3] reported rate coefficients for reaction (1) using a relative rate technique over the temperature range 253–328 K with pentane and cyclohexane as reference compounds. The results obtained with the different reference compounds agreed to within ±6%, or better. The results from the Chen et al. study are included in Fig. 5 for comparison with the present work. Their results are systematically lower than the present results (~9% lower at 298 K), but agree to within the combined estimated uncertainties over the temperature range common to both studies. Note that Chen et al. [3] and Baasandorj et al. [2] have each briefly discussed of the reactivity trends for fluorinated ethylenes.

OH Radical Regeneration

In this study, OH radical regeneration was observed under certain experimental conditions. In this section, we summarize our observations and identify several of the key parameters that impact OH radical formation, which are based on our rate coefficient and OH radical isotope temporal profile measurements in the presence and absence of O₂. Our experimental observations are consistent with the OH radical regeneration hypothesis presented in our previous study of the analogous OH + CH₂=CHF and CH₂=CF₂ reactions [2]. It is worth noting at this point that OH regeneration was not observed in our previous kinetic studies of several larger HFOs [5,8].

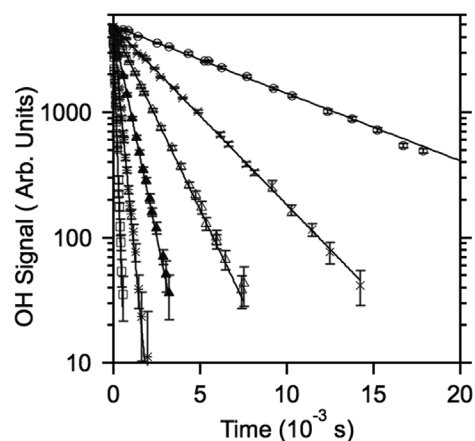
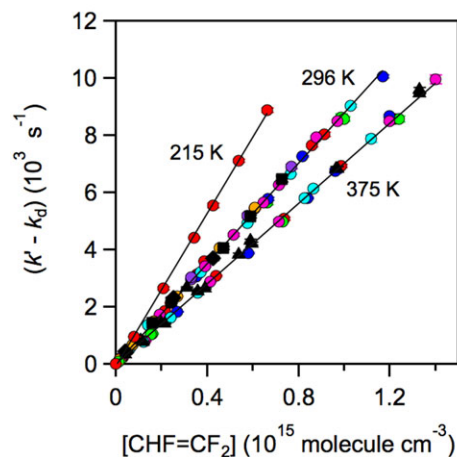
The mechanism and magnitude of the OH radical regeneration was investigated by variation of the experimental conditions and isotopic composition of the OH radical. Figure 4 shows OH radical temporal profiles that illustrate some of the key experimental observations outlined below:

Table III Summary of Experimental Conditions and Rate Coefficients Obtained for the Reaction of ^{18}OH and OD with $\text{CHF}=\text{CF}_2$

$T(\text{K})$	$P(\text{Torr, He})$	V $P(\text{Torr, He})$	Photolysis Laser Fluence ($\text{mJ cm}^{-2} \text{ pulse}^{-1}$)	$[\text{O}_3]$ ($10^{12} \text{ molecule cm}^{-3}$)	$[\text{H}_2\text{O}]^a/[\text{O}_2]$ ($10^{16} \text{ molecule cm}^{-3}$)	$[\text{OH}]_0$ ($10^{12} \text{ molecule cm}^{-3}$)	$[\text{CHF}=\text{CF}_2]$ ($10^{14} \text{ molecule cm}^{-3}$)	k^b ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$^{18}\text{OH} + \text{CHF} = \text{CF}_2$								
296	25	12	3.8	8.58	1.4/–	0.9	0.41–7.29	8.79 ± 0.13
296	25	12	3.8	8.58	1.4/–	0.9	0.41–4.26	8.77 ± 0.32
374	22	5.6	10.4	24.8	3.1/–	6.9	1.09–13.30	$k_{\text{Global}}(296 \text{ K}) = 8.77 \pm 0.16^c$
374	22	5.6	10.4	24.8	3.1/4.4	6.9	1.20–13.30	7.10 ± 0.04 7.00 ± 0.08 $k_{\text{Global}}(374 \text{ K}) = 7.10 \pm 0.15^c$
$\text{OD} + \text{CHF} = \text{CF}_2$								
296	20	7.3	7.8	14.0	2.37/–	3.0	0.40–8.80	8.89 ± 0.11
296	20	7.3	7.8	14.0	2.37/3.5	3.0	1.39–12.10	8.80 ± 0.10
373	24	6.4	1.8	15.3	2.82/–	7.6	0.48–12.40	$k_{\text{Global}}(296 \text{ K}) = 8.95 \pm 0.08^c$ 7.53 ± 0.11

^aEstimated H_2^{18}O or D_2O concentration.^bThe quoted uncertainties are the 2σ precision.^cGlobal rate coefficients were determined from a weighted linear least-squares fit of all $(k' - k_d)$ data obtained at a given reaction temperature versus the $\text{CHF}=\text{CF}_2$ concentration.

1. The measured ^{16}OH temporal profiles deviated from a simple pseudo-first-order decay, where the deviation (curvature) was only observed at total pressures < 100 Torr (He). OH regeneration is most likely not due to the dissociation of the $\text{OH-CHF}=\text{CF}_2$ adduct radical back to reactants.

**Figure 2** Representative OH temporal profiles measured in the $\text{OH} + \text{CHF}=\text{CF}_2$ reaction at 296 K and 300 Torr (He) in the absence of O_2 with $\text{CHF}=\text{CF}_2$ concentrations of 0, 0.26, 0.61, 1.41, 3.73, and $10.3 (10^{14} \text{ molecule cm}^{-3})$ in order of increasing decay rate. The lines are the weighted linear least-squares fits of the data to Eq. (I). The data error bars are 2σ of the measurement precision.**Figure 3** Second-order plot for the $\text{OH} + \text{CHF}=\text{CF}_2$ reaction at 296 K and the temperature extremes included in this study. The data set includes measurements made at pressures ≥ 100 Torr (He, N_2) for ^{16}OH (colored circles) and at all pressures for ^{18}OH (black squares, triangles, and diamonds). The lines are linear least-square fits of the data (including both ^{16}OH and ^{18}OH data). A summary of the rate coefficient results is given in Tables II and III.

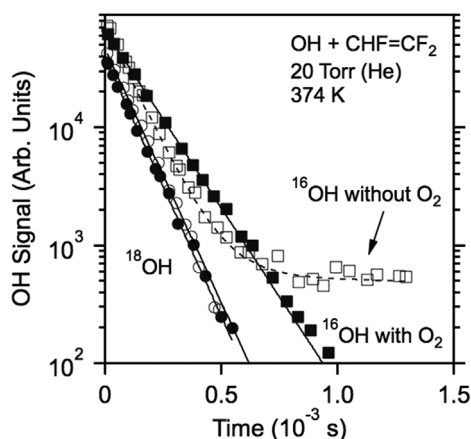


Figure 4 OH temporal profiles measured for the OH + CHF=CF₂ reaction at 374 K in 20 Torr (He) for ¹⁶OH and ¹⁸OH with and without O₂ added to the reaction mixture; ¹⁶OH (□, [O₂] = 0; ■ [O₂] = 2.6 × 10¹⁶ molecule cm⁻³) and ¹⁸OH (○, [O₂] = 0; • [O₂] = 2.6 × 10¹⁶ molecule cm⁻³) with [CHF=CF₂] = 1.35 × 10¹⁵ molecule cm⁻³. The solid lines are the weighted linear least-squares fits of the data to Eq. (1). The dashed line is a biexponential fit of the ¹⁶OH data in the absence of O₂. Data error bars are not shown for improved clarity of the profiles.

2. The magnitude of the OH regeneration increased with increasing temperature.
3. The ¹⁶OH temporal profile was dependent on the addition of O₂, where the addition of O₂ led to ¹⁶OH profiles that displayed pseudo-first-order behavior.
4. The ¹⁶OH pseudo-first-order rate coefficient in the presence of O₂ was less than obtained at pressures >100 Torr (He) and also less than measured for ¹⁸OH and OD, which implies the presence of regeneration.
5. The ¹⁸OH and OD temporal profiles were strictly pseudo-first order.
6. The ¹⁸OH and OD pseudo-first-order rate coefficients were independent of the addition of O₂.
7. ¹⁶OH radical formation was observed in the OD experiments, which implies the H-atom in the regenerated ¹⁶OH originates from the CHF=CF₂ molecule.
8. Under identical experimental conditions ¹⁶OH regeneration was observed, whereas ¹⁸OH regeneration was not observed (note that the ¹⁸OH radical source produces equivalent amounts of ¹⁶OH and ¹⁸OH initially). This implies that the rate coefficient derived from the ¹⁸OH radical decay represents the true reaction rate coefficient.

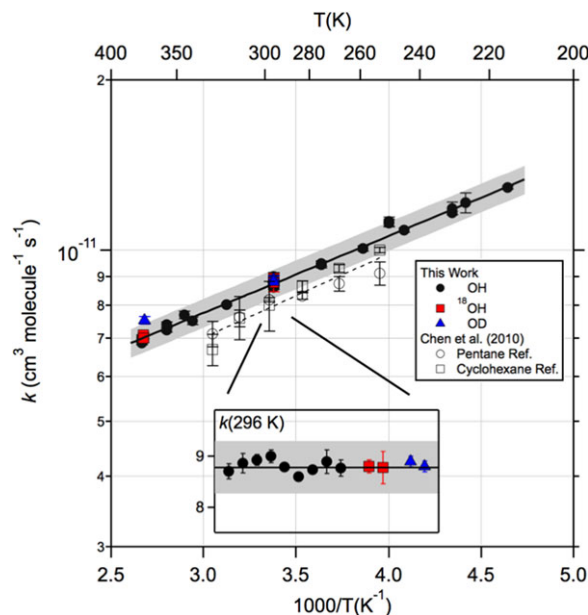


Figure 5 Arrhenius plot of the rate coefficients measured in this work for the reaction of ¹⁶OH, ¹⁸OH, and OD with CHF=CF₂ (see Tables II and III). The solid line is a weighted least-squares fit to our combined data sets. The inset shows an expanded view of the *k*(296 K) data from this work. The shaded region represents the range of a 1.06 uncertainty factor in *k* at all temperatures. The rate coefficient results from the relative rate study of Chen et al. [3] are included for comparison (see Legend for reference compound used), and the dashed line is a fit to their data. The error bars are the measurement precision.

Overall, OH regeneration in reaction (1) was a minor process. On the basis of the observed OH decay rates observed in the presence and absence of O₂, the OH yields in the OH ± CHF=CF₂ reaction at 20 Torr (He) were estimated to be ~10% at 296 K and ~15% at 375 K. The OH regeneration is less than was observed for the OH + CH₂=CF₂ and CH₂=CHF reactions in our previous study, 15 and 30% at 296 K and ~40 and 45% at 373 K, respectively [2]. That is, the magnitude of the OH regeneration decreased with increasing ethylene fluorination.

The absence of ¹⁸OH and OD regeneration is direct evidence that unimolecular dissociation of the stabilized OH-CHFCF₂ radical adduct back to reactants under our conditions was not a significant source of the observed OH regeneration. The OH-CHFCF₂ radical adduct is expected to be ~25 kcal mol⁻¹ stabilized relative to reactants [9] and, therefore, thermally stable under the present conditions.

The increase in the rate of OH regeneration upon O₂ addition implicates the role of the hydroxyperoxy

radical, OH-CHF₂-O₂, in the regeneration mechanism. The hydroxyperoxy is expected to be thermally stable on the timescale of our experiments, although experimental or theoretical heats of formation are not available for this species. In our previous study, we proposed that the observed OH regeneration is most consistent with a mechanism involving an energized hydroxyperoxy radical due to the decreased OH yield at lower temperatures and higher bath gas pressure. The present measurements also support such a mechanism. The mechanism may involve a H-atom isomerization followed by OH elimination as the observation of OH regeneration in the OD experiment would imply that the H-atom originates from the parent molecule. A theoretical analysis of the OH + hydrofluoroethene reactions in the presence of O₂ would provide valuable insight into the mechanism and dynamics for OH radical formation in this relatively simple but surprisingly complex reaction system, but is beyond the scope of the present study.

SUMMARY

Rate coefficients for the OH + CHF=CF₂ reaction were measured over a range of temperature 212–375 K at total pressures between 20 and 500 Torr (He, N₂). The rate coefficients were independent of pressure and are well represented by the Arrhenius expression $k_1(T) = (3.04 \pm 0.30) \times 10^{-12} \exp[(312 \pm 25)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with a measured room temperature rate coefficient of $k_1(296 \text{ K}) = (8.77 \pm 0.80) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The quoted uncertainty limits include estimated systematic errors.

Using the 272 K rate coefficient and an OH concentration of $1 \times 10^6 \text{ molecule cm}^{-3}$ leads to an atmospheric lifetime of ~ 1 day. CHF=CF₂ is, therefore, a very short-lived substance (VSLs), and its atmospheric lifetime will depend greatly on the location and time of its emission. Atmospheric loss processes for

CHF=CF₂ other than the OH reaction are expected to be minor, but if active would lead to a shorter lifetime. The tropospheric degradation of CHF=CF₂ would lead to the stoichiometric formation of CF₂O and HC(O)F as stable end-products irrespective of the OH radical addition site. The stable end-products are expected to be removed from the troposphere within days by deposition and hydrolysis processing [10]. Overall, the atmospheric oxidation of CHF=CF₂ has a neutral impact on the HO_x (HO_x = OH + HO₂) atmospheric budget.

The radiative efficiency (RE) for CHF=CF₂ was calculated to be $0.109 \text{ W m}^{-2} \text{ ppb}^{-1}$ using the methods given in Hodenbrog et al. [11] and the atmospherically well-mixed gas scenario. Using their VSLS emission scenario parameterization, a RE of $1.53 \times 10^{-3} \text{ W m}^{-2} \text{ ppb}^{-1}$ is obtained. Although the infrared absorption spectra for the fluoroethylenes have significant differences in band centers and band strengths, their estimated well-mixed REs agree to within $\sim 20\%$, where the REs for CH₂=CHF, CH₂=CF₂, and CF₂=CF₂ are 0.084 [2], 0.086 [2], and 0.114 [12] $\text{W m}^{-2} \text{ ppb}^{-1}$, respectively. The GWPs of CHF=CF₂ were calculated relative to CO₂ over 20, 100, and 500-year time horizons using the well-mixed and VSLS RE values are given in Table IV. The GWPs obtained for CHF=CF₂ are significantly less than those of saturated HFCs due primarily to its much shorter atmospheric lifetime. For example, the GWP for HFC-134a, CH₂FCF₃, a commonly used refrigerant, is 1300 over the 100-year time horizon [1] compared to 3.92×10^{-3} for CHF=CF₂.

The OH regeneration observed in this study was also observed in our previous studies of the OH + CH₂=CHF and CH₂=CF₂ reactions. The magnitude of the OH radical regeneration was found to decrease with increasing ethylene fluorination and displayed behavior that is consistent with a mechanism involving isomerization of a peroxy reaction intermediate. It should be noted that OH radical regeneration was not observed in our kinetic studies of C3 and C4

Table IV Global Warming Potentials of CHF=CF₂

Lifetime ^a (days)	Radiative Efficiency ($\text{W m}^{-2} \text{ ppb}^{-1}$)	Global Warming Potential ^b Time Horizons (years)		
		20	100	500
1.2	0.109 ^c	0.99 ^c	0.28 ^c	0.09 ^c
	0.00153 ^d	0.014 ^d	0.00392 ^d	0.00126 ^d

^aLifetime calculated for OH reactive loss using the rate coefficient at 272 K determined in this work and an OH concentration of $1 \times 10^6 \text{ molecule cm}^{-3}$.

^bGWPs calculated relative to CO₂.

^cCalculated assuming a CHF=CF₂ is well mixed in the atmosphere.

^dCalculated for CHF=CF₂ as a very short-lived substance (VSLs) using the fractional correction parameterization given in Hodenbrog et al. [11], correction factor = 0.014.

hydrofluoroolefins under similar experimental conditions [5,8]. The OH radical regeneration observed in reaction (1) is expected to be negligible under tropospheric boundary layer conditions.

BIBLIOGRAPHY

1. World Meteorological Organization. Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project-Report No. 55, 2014. Available at http://www.wmo.int/pages/prog/arep/gaw/ozone_2014/ozone_asst_report.html.
2. Baasandorj, M.; Knight, G.; Papadimitriou, V. C.; Talukdar, R. K.; Ravishankara, A. R.; Burkholder, J. B. *J Phys Chem A* 2010, 114, 4619–4633.
3. Chen, L.; Uchimaru, T.; Kutsuna, S.; Tokuhashi, K.; Sekiya, A. *Int J Chem Kinet* 2010, 42, 619–628.
4. Davis, M. E.; Burkholder, J. B. *Atmos Chem Phys* 2011, 11, 3347–3358.
5. Papadimitriou, V. C.; Talukdar, R. K.; Portmann, R. W.; Ravishankara, A. R.; Burkholder, J. B. *Phys Chem Chem Phys* 2008, 10, 808–820.
6. Baasandorj, M.; Papanastasiou, D. K.; Talukdar, R. K.; Hasson, A. S.; Burkholder, J. B. *Phys Chem Chem Phys* 2010, 12, 12101–12111.
7. Burkholder, J. B.; Sander, S. P.; Abbatt, J.; Barker, J. R.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Orkin, V. L.; Wilmouth, D. M.; Wine, P. H. “Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18,” JPL Publication 15–10, Jet Propulsion Laboratory, Pasadena, CA, 2015. Available at <http://jpldataeval.jpl.nasa.gov/>, 2015.
8. Baasandorj, M.; Ravishankara, A. R.; Burkholder, J. B. *J Phys Chem A* 2011, 115, 10539–10549.
9. Papadimitriou, V. C.; Lazarou, Y. G.; Talukdar, R. K.; Burkholder, J. B. *J Phys Chem A* 2011, 115, 167–181.
10. Burkholder, J. B.; Cox, R. A.; Ravishankara, A. R. *Chem Rev* 2015, 115, 3704–3759.
11. Hodnebrog, Ø.; Etminan, M.; Fuglestvedt, J. S.; Marston, G.; Myhre, G.; Nielsen, C. J.; Shine, K. P.; Wallington, T. *J Rev Geophys* 2013, 51, 300–378.
12. Drage, E. A.; Jaksch, D.; Smith, K. M.; McPheat, R. A.; Vasekova, E.; Mason, N. J. *J Quant Spectrosc Radiat Transfers* 2006, 98, 44–56.